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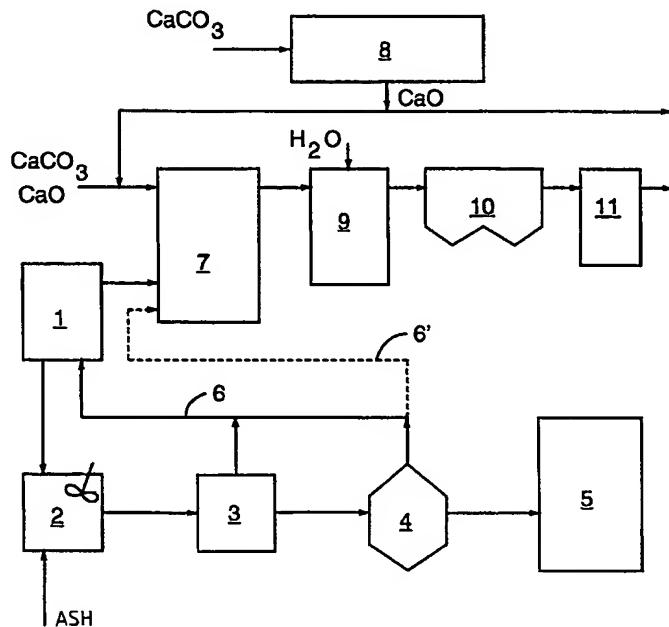
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(54) Titre : METHODE POUR AJUSTER LE RAPPORT S/Na DANS UNE USINE DE PATE AU SULFATE
(54) Title: METHOD FOR ADJUSTING THE S/Na RATIO IN A SULPHATE PULP MILL



(57) Abrégé/Abstract:

The invention relates to a method for adjusting the S/Na ratio at a sulphate pulp mill, wherein sulfur is separated from the chemical recovery loop as sulfurous odor gases. In the invention, the odor gases are passed into a power boiler (7) of the mill to be burned therein and they are neutralized by feeding calcium oxide generated in a lime kiln into the power boiler (7) from the kiln.



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Abstract

The invention relates to a method for adjusting
the S/Na ratio at a sulphate pulp mill, wherein
5 sulfur is separated from the chemical recovery
loop as sulfurous odor gases. In the invention,
the odor gases are passed into a power boiler
(7) of the mill to be burned therein and they
are neutralized by feeding calcium oxide
10 generated in a lime kiln into the power boiler
(7) from the kiln.
(Fig. 1)

Method for adjusting the S/Na ratio in a sulphate pulp mill

The invention relates to a method for adjusting
5 sulfur concentration in a sulphate pulp mill by
removing cumulated sulfur from the chemical recovery
loop, wherein sulfur is removed from black liquor in
the form of sulfurous odor gases separated from the
black liquor during treatment.

10 In the production of sulphate pulp, wood is
treated with alkaline cooking liquor, whereby lignin
contained in the wood is dissolved in the liquor and
cellulosic fibres are released. After cooking, the
cellulosic fibres are separated from the liquor, and
15 the black liquor containing lignin is passed into
further treatment and back into the chemical recovery
loop. Black liquor is first concentrated by evaporat-
ing water from it, and the concentrated black liquor
is burned in a soda recovery boiler. Salt smelt
20 obtained from burning, containing mainly Na_2S and
 Na_2CO_3 , is dissolved in water, thus obtaining green
liquor. Green liquor is causticized with slaked lime,
that is, calcium oxide, thus obtaining white liquor
and CaCO_3 , that is, calcium carbonate. White liquor is
25 recycled into pulp cooking, and calcium carbonate is
passed into a lime kiln, where it is again calcined
into calcium oxide needed in causticization.

Sulfur is introduced into the chemical recovery
loop and process of sulphate pulp e.g. from sulfuric
30 acid used in soap splitting. Part of the sulfur is
usually emitted with flue gases in the form of sulfur
dioxide and part remains in the chemical recovery
loop. For environmental reasons, attempts are made to
reduce the amount of sulfur compounds released with
35 flue gases by using e.g. a scrubber, as a result of

which the amount of sulfur gathered in the chemical recovery loop is correspondingly greater, as the solution leaving the scrubber has absorbed sulfur, and it is usually recycled into the cooking solution. The 5 amount of sulfur compounds in flue gases can be reduced in many ways. One way is to increase the solids content of black liquor. Sulfur compounds are present not only in flue gases but also in odor gases separated at different stages at the pulp mill and in flash 10 gases from the last concentration stage. Such sulfur compounds include H_2S , CH_2HS , $(CH_3)S_2$, $(CH_3)_2S$ and $(CH_3)_2S_2$. These odor gases are usually burned in a separate waste heat boiler or in a lime kiln. Burning 15 in the waste heat boiler results in sulfur dioxide, which has to be removed from the flue gases of the waste heat boiler by means of a separate scrubber. Burning odor gases in the lime kiln requires a separate odor gas burner, in addition to which the reactions of sulfur and lime deteriorate the calcination process of the lime kiln.

Attempts have been made to remove sulfur from the sulphate cellulose process by using waste lime obtained from lime reburning. This has been done by treating the sulfur dioxide obtained in the burning of 25 odor gases with a $NaOH$ solution, and the obtained sodium bisulphite is treated with calcium oxide, resulting in solid calcium sulphite and calcium sulphate. This method disclosed in FI Patent Application 920 531, a so-called dual-alkaline process, is 30 very complicated and difficult to realize.

The object of the present invention is to remove sulfur from the chemical recovery loop of a pulp mill in such a way that a desired S/Na ratio can be maintained. According to the invention, the odor gases are 35 passed into a power boiler at the pulp mill to be

burned there, calcium oxide produced in a lime kiln is introduced into the power boiler from the kiln in an amount such that at least sulfur compounds generated from the odor gases and calcium oxide react forming 5 calcium sulphite and calcium sulphate so that they can be removed from the flue gases as dry dust-like reaction products.

The essential idea of the invention is that odor gases containing various sulfur compounds are passed 10 into a power boiler to be burned there while introducing calcium oxide from the lime kiln into the power boiler. Calcium oxide binds sulfur compounds generated in the boiler during burning into a solid reaction product that can be separated in dust form. According 15 to one preferred embodiment of the invention, odor gases containing sulfur compounds are first passed into an evaporation plant and only then into the power boiler, which allows the thermal energy of the odor gases to be utilized in the evaporation plant.

20 An advantage of the method according to the invention is that the desulfuration process can utilize the existing equipment and material of the pulp mill, and no separate auxiliary devices are needed. Another advantage is that the method is simple 25 and easy to apply at existing pulp mills and its investment costs are low.

The invention will be described more fully with reference to the attached drawings, where

30 Figure 1 is a block diagram illustrating the method according to the invention;

Figure 2 is a block diagram illustrating a second embodiment of the method according to the invention; and

35 Figure 3 illustrates a third embodiment of the method according to the invention.

Figures 1 to 3 are block diagrams illustrating sections of the pulp cooking process to such an extent as is necessary for the understanding of the invention. In other respects, the sulphate pulp cooking process is known *per se* and obvious to one skilled in the art, and therefore it will not be described more closely. In Figures 1 to 3, the same process sections are indicated with the same reference numerals, which will be explained mainly with reference to Figure 1.

In describing the other figures, the reference numerals are further explained only when this is necessary for the concerned embodiment of the invention.

Figure 1 illustrates an evaporation plant 1, into which black liquor is introduced in order that water could be removed from it, thus concentrating the black liquor. From the evaporation plant the black liquor is passed into a mixing tank 2, where ash is mixed with it. From the mixing tank 2, the black liquor is further passed into a final concentration stage 3, where the dry solids content of the black liquor is increased by up to 80% and even more at a pressure exceeding atmospheric pressure and at a temperature exceeding 100°C. From the final concentration stage 3, the black liquor is further passed into a flash tank 4, where it is allowed to expand so that more steam and sulfurous gases will be released. From the flash tank 4, the black liquor is passed into a soda recovery boiler 5, where it is burned so as to recover chemicals.

Steam and odor gases leaving the final concentration stage 3 and the flash tank 4 can be carried through a line 6 to the evaporation plant, where their thermal energy is utilized in the evaporation of black liquor. The steam and the odor gases entrained in it

may also be fed directly into the power boiler through a line 6' indicated with a broken line in the figure. Odor gases from the evaporation plant 1 are also carried into the power boiler 7 to be burned there,
5 whereby the gases produce sulfur oxides, mainly sulfur dioxide, in the power boiler 7. The power boiler 7 may be of any type, including various circulating fluidized bed boilers, fluidized bed boilers or grate boilers, which usually burn wood bark, a fuel abundantly available at a pulp mill, or some other suitable material.
10

Sulfur oxides produced in the power boiler 7 can be removed in different ways. According to one embodiment of the invention, calcium oxide produced in a lime kiln 8 and, if required, also additional calcium carbonate is introduced into the power boiler 7 in order to remove oxides generated in the burning of sulfur introduced together with in the fuel and odor gases. In the power boiler 7, calcium oxide or the
15 calcium oxide formed in the burning of calcium carbonate react partly with sulfur oxides, which yields calcium sulphite or calcium sulphate. From the power boiler 7 they are carried with flue gases e.g. into a separate desulfuration reactor 9, where water
20 is introduced into the flue gases. Calcium oxide that has not reacted in the boiler is thus hydrated into calcium hydroxide and it reacts actively with the remaining sulfur oxides at the same time. The dust-like reaction product leaving the desulfuration
25 reactor 9 with the flue gases is separated by an electrostatic precipitator 10. If required, rest of the flue gases can be passed into a gas scrubber 11, where they are washed with a NaOH solution and then passed into a chimney.
30

35 The essential aspect of the invention is that

odor gases from all process steps are passed into the power boiler to be burned there and the resulting sulfur oxides are removed from the flue gases by introducing calcium oxide produced in the lime kiln 5 into the power boiler. In this way the thermal energy of the flue gases can be utilized in different ways, in addition to which the entire process can directly use material that the mill anyway produces, i.e. calcium oxide. No separate waste heat boiler is thus 10 needed nor does the desulfuration disturb the burning process in the lime kiln, as the lime required for the neutralization of sulfur is taken from the lime kiln only after lime reburning and no substances disturbing the process are introduced into the kiln.

15 Figure 2 in turn illustrates another embodiment of the invention, which deviates from that shown in Figure 1 only with respect to the section after the power boiler 7. In this embodiment, calcium oxide from the lime kiln 8 is mixed with water in a separate 20 mixing tank 12 so that calcium hydroxide is obtained. Calcium hydroxide solution in turn is passed into the gas scrubber 11, into which flue gases from the power boiler 7 are also passed. In this embodiment, dust contained in the flue gases can also be removed with 25 the calcium hydroxide solution, so that no separate dust filter shown in Figure 1 is necessarily needed. After the scrubber, the flue gases can be passed directly into the chimney.

30 Figure 3 shows a third embodiment according to the invention, where a separate thermal treatment stage 13 for black liquor is added to the arrangement shown in Figure 1 after the final concentration stage 3. In this thermal treatment stage, black liquor is treated at a pressure exceeding atmospheric pressure 35 and at a temperature exceeding the cooking temperature

before it is introduced into the flash tank 4. In this embodiment, the amount of sulfur to be removed can be adjusted by varying the temperature and duration of the thermal treatment. This allows desulfurization to be
5 optimized in view of the sulfur accumulation of the process. The thermal treatment as such is well-known e.g. from FI Patent Application 921 444. In this embodiment of the invention it is also possible to
10 use the calcium hydroxide wash illustrated in Figure 2 in place of the separate desulfurization reactor.

The invention has been described above and shown in the drawings by means of example, and it is not in
15 any way restricted to it. It is essential that odor gases generated in the process are passed into the power boiler to be burned therein, and sulfur oxides formed in the power boiler are neutralized by introducing calcium oxide produced in the lime kiln into
20 the power boiler. In addition, calcium oxide from the lime kiln is possibly used in the form of calcium hydroxide solution for washing flue gases. It is to be noted that when the power boiler is a circulating fluidized bed boiler, desulfurization in the power
25 boiler is so efficient that no separate humidification reactor is needed. If desired, this embodiment may also use washing with calcium hydroxide solution for the final washing of flue gases.

Claims:

1. Method for adjusting sulfur concentration in a sulphate pulp mill by removing cumulated sulfur from the chemical recovery loop, wherein sulfur is removed from black liquor in the form of sulfurous odor gases separated from the black liquor during treatment, the odor gases are passed into a power boiler at the pulp mill to be burned there, calcium oxide produced in a lime kiln is introduced into the power boiler from the kiln in an amount such that sulfur compounds generated from the odor gases and calcium oxide react forming calcium sulphite and calcium sulphate so that they can be removed from flue gases as dry dust-like reaction products.

2. Method according to claim 1, wherein flue gases from the power boiler and calcium oxide that is still unreacted after the power boiler are passed together with the flue gases into a separate reactor where they are humidified with water, whereby the unreacted calcium oxide reacts with water, thus forming calcium hydroxide, which correspondingly reacts with sulfur oxides that are still unreacted.

3. Method according to claim 1, wherein calcium oxide is mixed with water to form calcium hydroxide, and sulfur-compounds-containing flue gases from the power boiler are passed into a gas scrubber, where they are washed with calcium hydroxide solution.

4. Method according to claim 1, wherein the removal of sulfur from a process is adjusted by using a separate thermal treatment stage in the treatment of black liquor, in which stage the black liquor is maintained at a temperature higher than that of the preceding treatment stages and at a pressure exceeding atmospheric pressure for a predetermined period of

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time and the black liquor is then allowed to expand so that a desired amount of sulfur will be removed from the black liquor in the form of odor gases.

5 5. Method according to claim 1, wherein the power boiler is a grate boiler in type.

6. Method according to claim 1, wherein the power boiler is a circulating fluidized bed boiler in type.

10 7. Method according to claim 1, wherein the power boiler is a fluidized bed boiler in type.

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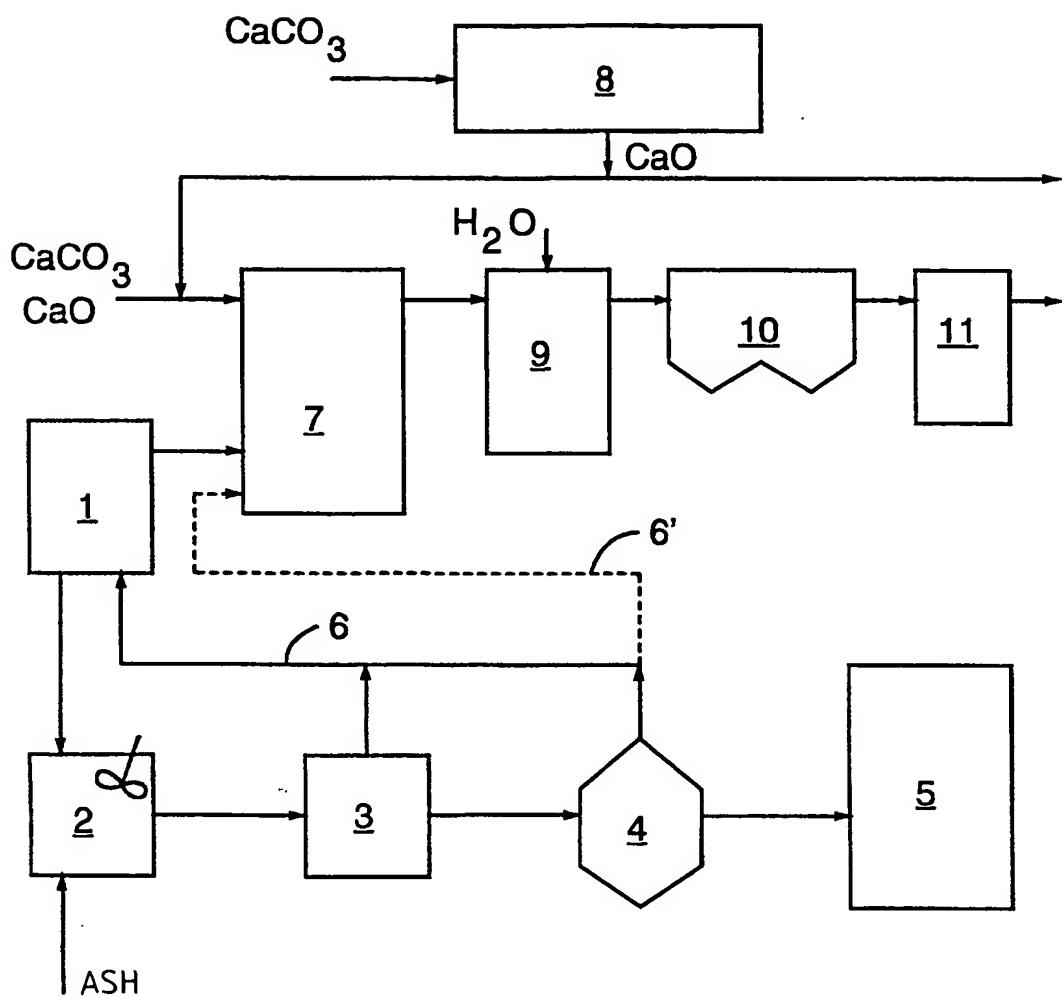
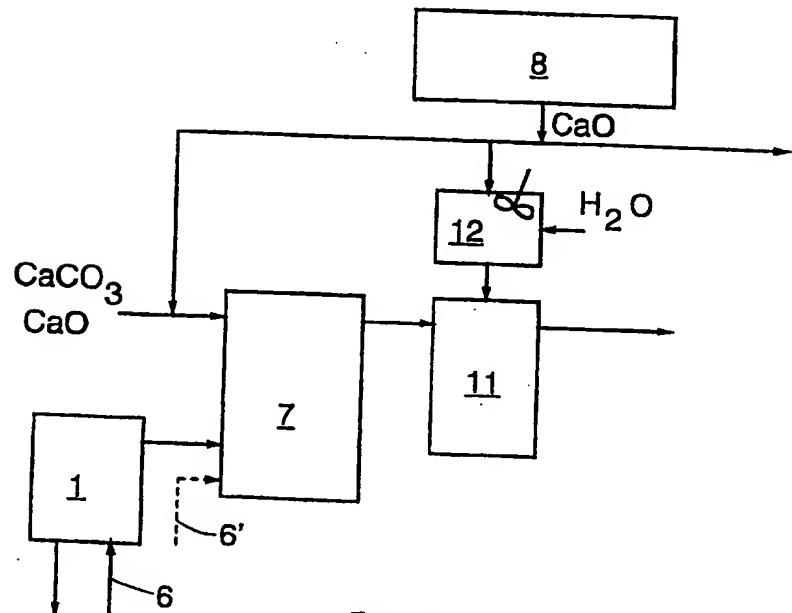
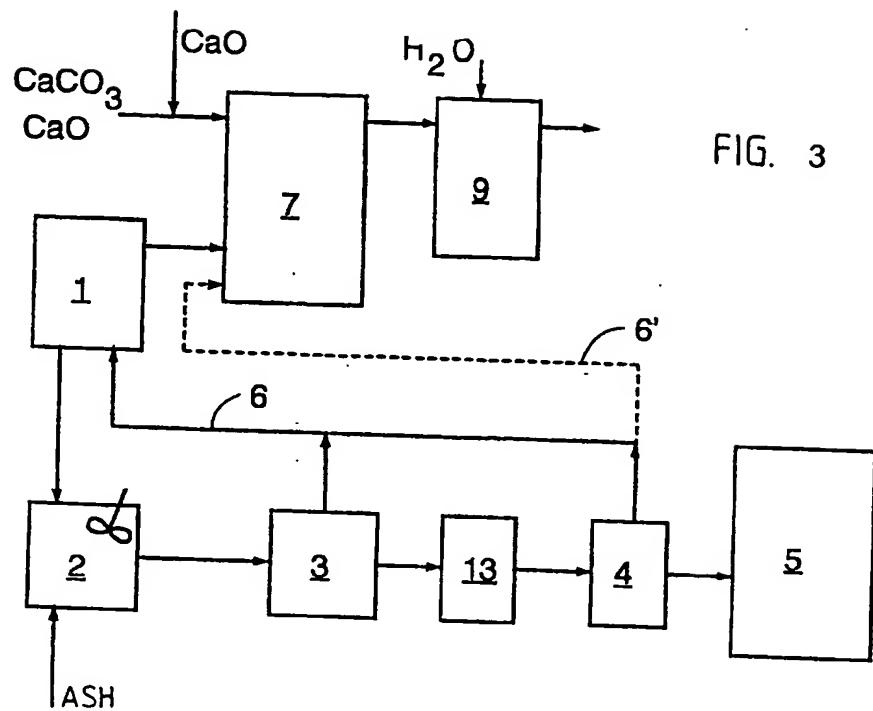


FIG. 1

Gowling, Strathy & Henderson



Gowling, Strathy & Henderson